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(21) International Application Number: PCT/EP00/03150 (22) International Filing Date: 8 April 2000 (08.04.00) (30) Priority Data: 09/291,961 15 April 1999 (15.04.99) US (71) Applicant (for all designated States except US): DYSTAR TEXTILFARBEN GMBH & CO. DEUTSCHLAND KG [DE/DE]; Eschenheimer Tor 2, D-60318 Frankfurt Am Main (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): PEDEMONTE, Ronald [US/DE]; Im Hirtengarten 7, D-65817 Epp- stein-Vockenhausen (DE). STROBEN, Andreas [DE/DE]; Herzogenfeld 27, D-51519 Odenthal (DE). DEL BUONO, Doriano [IT/DE]; Meisenweg 14, D-51373 Leverkusen (DE).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: DEEP NAVY DYE MIXTURES OF FIBER-REACTIVE AZO DYES AND A METHOD FOR THEIR PREPARATION AND A PROCESS FOR DYEING HYDROXY AND/OR CARBOXAMIDO CONTAINING FIBERS (57) Abstract The present invention comprises a dye mixture comprising one or more, such as one, two or three, disazo dyes conforming to general formula (1), one or more, such as one, two or three, monoazo dyes conforming to general formula (2), in which (1) and (2) are defined as given in claim 1, a method for its preparation and a process for dyeing hydroxy- and/or carboxamido containing fiber material in which an inventive dye is applied to the material.		

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Description

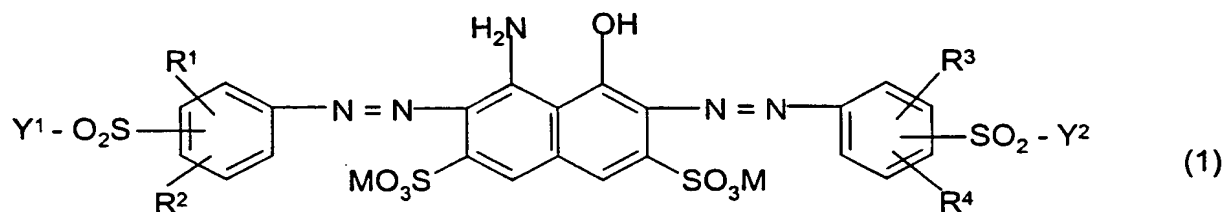
- 5 Deep Navy Dye Mixtures of Fiber-Reactive Azo Dyes and A Method for their Preparation and A Process for Dyeing Hydroxy and/or Carboxamido Containing Fibers

The present invention relates to the field of fiber-reactive dyes.

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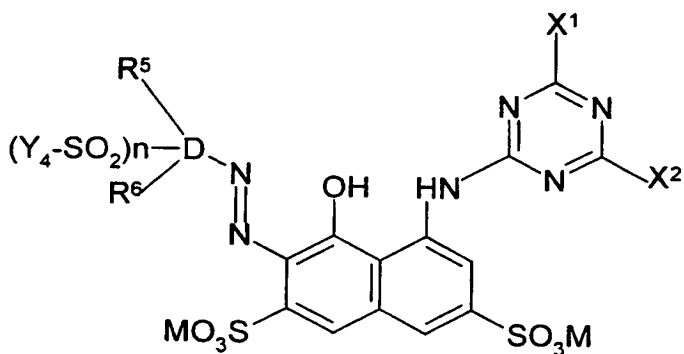
Navy-dyeing mixtures of fiber-reactive dyes are known from European Patent Applications EP-A 0588257, EP-A 0668328, EP-A 0127456. However these dye mixtures have still some deficiencies, such as, for ex., when applied to substrates other than cellulose, for example wool. Deep navy shades on carboxamido
 15 containing fibers are usually achieved by the application of mordant dyes. Mordant dyes are well known for their good fastness - and dyeing properties. However they have ecological disadvantages, so that alternative reactive dye mixtures are desirable.

- 20 With the present invention, deep navy-dyeing reactive dye mixtures have been found which unexpectedly and surprisingly have improved properties, such as improved resistance to ammonium aftertreatment and levelness in regard to the dyeing of wool. The present invention discloses dye mixtures comprising one or more, such as one, two or three, disazo dyes conforming to the general formula (1)



one or more, such as one, two, three or four, monoazo dyes conforming to the general formula (2),

30



(2)

in which:

R^1 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy, preferably methoxy or hydrogen and in particular hydrogen;

R^2 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy, preferably hydrogen;

R^3 has one of the meanings of R^1

R^4 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy, preferably hydrogen;

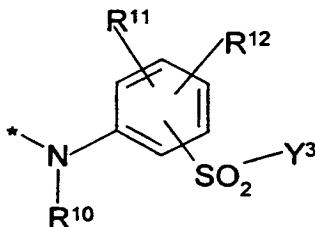
R^5 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy, preferably methoxy, sulfo or hydrogen and in particular sulfo;

R^6 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy, preferably methoxy, sulfo or hydrogen and in particular sulfo;

D is a benzene or naphthalene radical;

n is 0 or 1

X^1 is a fluoro, chloro, cyanamido, or morpholino group or a group of the following formulae; NR^7R^8 or OR^9 or wherein



R^7 is hydrogen, methyl, ethyl, hydroxyethyl, methoxyethyl, ethoxyethyl, or sulfoethyl, preferably ethyl, methoxyethyl, sulfoethyl

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- R^8 has one of the meanings of R^7 ;
 R^9 has one of the meanings of R^7 ;
 R^{10} has one of the meanings of R^7 ;
 R^{11} is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy, preferably
5 methoxy or hydrogen and in particular hydrogen;
 R^{12} is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy, preferably
methoxy or hydrogen and in particular hydrogen;
 X^2 has one of the meanings of X^1 ;
 Y^1 is vinyl, or is ethyl substituted in the β -position by a substituent which is
10 eliminated by the action of an alkali, forming the vinyl group, such as chlorine,
thiosulfato, sulfato, alkanoyloxy of 2 to 5 carbon atoms, such as acetyloxy,
phosphato, sulfobenzoyloxy and p-toluylsulfonyloxy, and Y^1 is preferably vinyl,
 β -chloroethyl, β -thiosulfatoethyl or β -sulfatoethyl and is in particular preferably
vinyl or β -sulfatoethyl;
15 Y^2 has one of the meanings of Y^1 ;
 Y^3 has one of the meanings of Y^1 ;
 Y^4 has one of the meanings of Y^1 ;
M denotes hydrogen or an alkali metal such as lithium, sodium and potassium.

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Both in the formulae mentioned above and in those below, the individual formula members, both with different and with the same designation within a formula or the various formulae, can within the scope of their definitions have meanings which are the same as or different from one another.

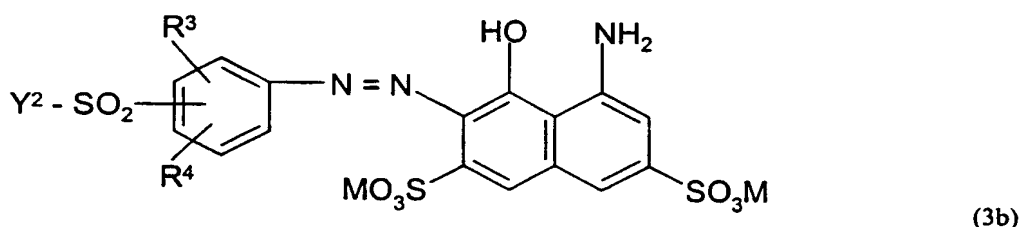
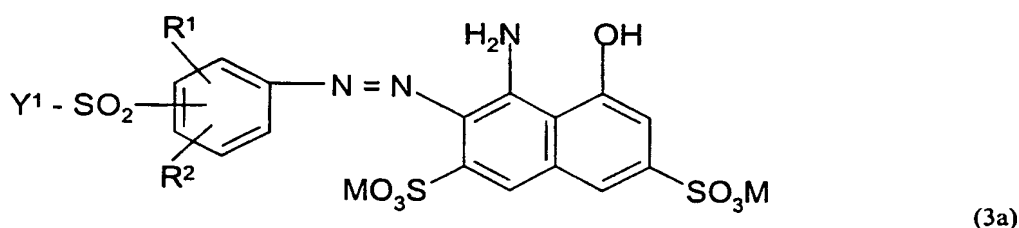
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The groups "sulfo", "thiosulfato", "carboxy", "phosphato" and "sulfato" include both the acid form and the salt form of these groups. Accordingly, sulfo groups are groups of the formula $-\text{SO}_3\text{M}$, thiosulfato groups are groups of the formula
30 $-\text{S}-\text{SO}_3\text{M}$, carboxy groups are groups of the formula $-\text{COOM}$, phosphato groups are groups of the formula $-\text{OPO}_3\text{M}_2$ and sulfato groups are groups of the formula $-\text{OSO}_3\text{M}$, in which M is defined as above.

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The dye, respectively dyes, of the general formula (1) are present in the mixtures in an amount of from 70 to 95% by weight, preferably of from 75 to 90 % by weight, and the dye, respectively dyes of the general formula (2) are present in the mixtures in an amount of from 5 to 30% by weight, preferably of from 10 to 25 % by weight.

The dye mixtures of the invention may optionally contain one, two or three dyestuffs corresponding to the general formula (3a) or (3b) or both



in which R^1 , R^2 , R^3 , R^4 , M , Y^1 and Y^2 are defined as above. These two monoazo dyestuffs may be already formed during the synthesis of the disazo dye of formula (1) when coupling reactions of the starting compounds are incomplete.

If the dye mixture of the instant invention contains, as a further component, a monoazo dyestuff of formula (3a) or of formula (3b) or both, the dye or dyes of formula (3a) or of formula (3b) or of both are present in the dye mixture of the dyes of formula (1) and (2) in the range of 0.01 to 8 % by weight, calculated on the 100 % dye mixture of the dyes (1) and (2).

The dyes of the general formulae (1), (2), (3a) and (3b), in particular if those corresponding to the same general formula have the same chromophore, can have, within the meaning of their Y -moiety, structurally different fiber-reactive groups

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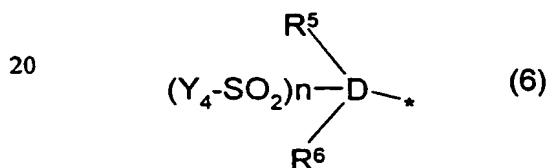
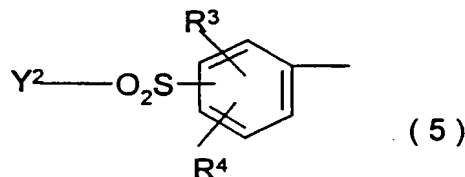
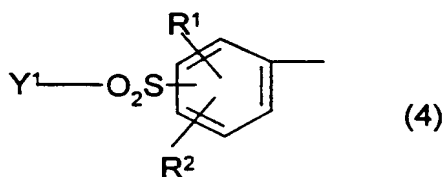
corresponding to their $-\text{SO}_2\text{-Y}$ -moiety. In particular, the dye mixture can contain dyes of the same chromophore conforming to the formula (1) and/or dyes of the same chromophore conforming to formula (2), optionally likewise of the general formula (3a) or (3b) or both in which the fiber-reactive groups of the corresponding

5 $-\text{SO}_2\text{-Y}$ -moiety are partly vinylsulfonyl groups and partly groups in which the Y-moiety is a β -ethyl substituted group as defined above, such as β -chloroethylsulfonyl, β -thiosulfatoethylsulfonyl or, preferably, β -sulfatoethylsulfonyl groups. If the dye mixtures contain the respective dye components in the form of a vinylsulfonyl dye, the proportion of the respective vinylsulfonyl dye to the respective

10 dye with a Y-moiety being a β -ethyl substituted group as defined above, such as a β -chloro- or β -thiosulfato- or β -sulfatoethyl-sulfonyl dye, will be up to about 30 mol-%, based on the respective dye chromophore. Preference is here given to the dye mixtures in which the proportion of vinylsulfonyl dye to said β -substituted ethylsulfonyl dye, such as β -sulfatoethylsulfonyl dye, is in terms of the molar ratio

15 between 2 : 98 and 30 : 70.

Radicals of the formulae (4), (5) and (6)



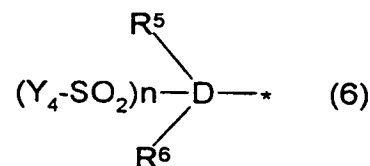
in the dyes of formulae (1), (2) for $n=1$, (3a) and (3b) are, for example,

25 2-(β -sulfatoethylsulfonyl)phenyl, 3-(β -sulfatoethylsulfonyl)phenyl, 3- or 4-vinylsulfonylphenyl, 4-(β -sulfatoethylsulfonyl)phenyl, 2-carboxy-5-(β -sulfatoethylsulfonyl)phenyl, 4-methoxy-3-(β -sulfatoethylsulfonyl)-phenyl, 2-ethoxy-4- or -5-(β -sulfatoethylsulfonyl)phenyl, 2-methyl-4-(β -sulfatoethylsulfonyl)-phenyl, 2-methoxy-5- or -4-(β -sulfatoethylsulfonyl)phenyl, 2,4-diethoxy-5-(β -sulfato-

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ethylsulfonyl)phenyl, 2,4-dimethoxy-5-(β -sulfatoethylsulfonyl)phenyl, 2,5-dimethoxy-4-(β -sulfatoethylsulfonyl)phenyl, 2-methoxy-5-methyl-4-(β -sulfatoethylsulfonyl)phenyl, 2- or 3- or 4-(β -thiosulfatoethylsulfonyl)phenyl, 2-methoxy-5-(β -thiosulfatoethylsulfonyl)phenyl, 2-sulfo-4-(β -phosphatoethylsulfonyl)phenyl, 2-sulfo-4-vinylsulfonylphenyl and 3- or 4-(β -acetoxylethylsulfonyl)phenyl and their corresponding vinylsulfonyl derivatives.

Radicals of the formula (6)



for $n=0$ in the dyes of formula (2) are, for example 4-methyl-2-sulfophenyl, 4-methoxy-2-sulfophenyl, 4-sulfophenyl, 3-sulfophenyl, 2-sulfophenyl, 4-methoxy-2,5-disulfophenyl, 4-methyl-2,5-disulfophenyl, 1,5-disulfonaphthyl or 1-sulfonaphthyl.

Preference is given to dye mixtures according to the invention, in which

D is the radical of 1,5-disulfonaphthyl

R¹ is methoxy or hydrogen,

R² is hydrogen,

R³ is methoxy or hydrogen,

R⁴ is hydrogen,

X¹ is chlorine

X² is the radical 4-(β -sulfatoethylsulfonyl)phenyl

and R¹, R², R³ and R⁴ are in particular preferred each hydrogen and the Y-moieties are each preferable, independently of the other one vinyl or β -sulfatoethyl.

The dye mixtures of the invention can be present as a preparation in solid or liquid (dissolved) form. In solid form they generally contain the electrolyte salts customary in the case of water-soluble and in particular fiber-reactive dyes, such as sodium chloride, potassium chloride and sodium sulfate, and also the assistants customary in commercial dyes, such as buffer substances capable of establishing a pH in aqueous solution between 3 and 7, such as sodium acetate, sodium borate, sodium

bicarbonate, sodium dihydrogenphosphate and disodium hydrogenphosphate, small amounts of siccatives or, if they are present in liquid, aqueous solution (including the presence of thickeners of the type customary in print pastes), substances which ensure the permanence of these preparations, for example mold preventatives.

5

If the dye mixtures take the form of dye powders, they contain, as a rule, 10 to 80 % by weight, based on the dye powder or preparation, of a strength-standardizing colorless diluent electrolyte salt, such as those mentioned above. These dye powders may in addition contain the abovementioned buffer substances in a total amount of up to 5 %, based on the dye powder. If the dye mixtures of the invention are present in aqueous solution, the total dye content of these aqueous solutions is up to about 50 % by weight, the electrolyte salt content of these aqueous solutions preferably being below 10 % by weight, based on the aqueous solutions (liquid preparations) can in general contain the abovementioned buffer substances in an amount of up to 5 % by weight, preferably up to 2 % by weight.

10

15

The dye mixtures of the invention are preparable in a conventional manner, as by mechanically mixing the individual dyes in the necessary proportions, whether in the form of their dye powders or granules or their synthesis solution or of aqueous solutions of the individual dyes in general, which may still include customary auxiliaries.

20

The dyes according to the general formula (1) are known from the U.S. Patents Nos. 2,657,205, 3,387,914, 4,072,463 and 4,257,770 or from one of the above-mentioned publications, and the dyes of the general formula (2) are known from the European Patent Application EP-A 534 342 and from the European Patent Application EP A 177 449.

25

The dye mixtures of the instant invention are well suitable for dyeing (which includes printing) hydroxy- and/or carboxamido-containing fiber materials by the application and fixing methods numerously described in the art for fiber-reactive dyes, in deep navy shades with good color build-up and good wash-off in respect of unfixed dye portions.

30

The present invention therefore also provides for use of the novel dye mixtures for dyeing (including printing) hydroxy- and/or carboxamido-containing fiber materials and processes for dyeing such fiber materials and processes for dyeing such materials using a dye mixture according to the invention by applying the dye mixture to the substrate in dissolved form and fixing the dyes on the fiber by the action of an alkali or by heating or both.

Hydroxy-containing materials are natural or synthetic hydroxy-containing materials, for example cellulose fiber materials, including in the form of paper, or their regenerated products and polyvinyl alcohols. Cellulose fiber materials are preferably cotton but also other natural vegetable fibers, such as linen, hemp, jute and ramie fibers; regenerated cellulose fibers are for example staple viscose and filament viscose.

Carboxamido-containing materials are for example synthetic and natural polyamides and polyurethanes, in particular in the form of fibers, for example wool and other animal hairs, silk, leather, nylon-6,6, nylon-6, nylon-11, and nylon-4.

Furthermore, the dye mixtures of the invention can also be used for the fiber-reactive dyeing of wool. Moreover, wool which has been given a nonfelting or low-felting finish (cf. H. Rath, Lehrbuch der Textilchemie, Springer-Verlag, 3rd Edition (1972), p. 295-299, especially the finish by the so-called Hercosett process (p. 298); J. Soc. Dyers and Colourists 1972, 93-99, and 1975, 33-44) can be dyed with very good fastness properties.

The process of dyeing on wool is here carried out in a conventional manner from an acidic medium. For instance, acetic acid and/or ammonium sulfate or acetic acid and ammonium acetate or sodium acetate may be added to the dyebath to obtain the desired pH. To obtain a dyeing of acceptable levelness, it is advisable to add a customary leveling agent, for example on the basis of a reaction product of cyanuric chloride with 3 times the molar amount of an aminobenzenesulfonic acid and/or of an aminonaphthalenesulfonic acid or on the basis of a reaction product of for example stearylamine with ethylene oxide. For instance, the dye mixture of the invention is

preferably subjected to the exhaustion process initially from an acidic dyebath having a pH of about 3.5 to 5.5 under pH control and the pH is then, toward the end of the dyeing time, shifted into the neutral and perhaps weakly alkaline range up to a pH of 8.5 to bring about, especially for very deep dyeings, the full reactive bond between the dyes of the dye mixtures of the invention and the fiber. At the same time, the dye portion not reactively bound is removed.

The procedure described herein also applies to the production of dyeings on fiber materials composed of other natural polyamides or of synthetic polyamides and polyurethanes. In general, the material to be dyed is introduced into the bath at a temperature of about 40°C, agitated therein for some time, the dyebath is then adjusted to the desired weakly acidic, preferably weakly acetic acid, pH and the actual dyeing is carried out at a temperature between 60 and 98°C. However, the dyeings can also be carried out at the boil or in sealed dyeing apparatus at temperatures of up to 106°C. Since the water solubility of the dye mixtures of the invention is very good, they can also be used with advantage in customary continuous dyeing processes. The color strength of the dye mixtures of the invention is very high.

Application of the dye mixtures of the invention is by generally known processes for dyeing and printing fiber materials by the known application techniques for fiber-reactive dyes. Since the dyes of the dye mixtures according to the invention are highly compatible with one another, the dye mixtures of the invention are also advantageously useful in exhaust dyeing processes. Applied in this way for example to cellulose fibers from a long liquor ratio at temperatures between 40 and 105°C, optionally at temperatures up to 130°C, under superatmospheric pressure, and optionally in the presence of customary dyeing assistants with the use of acid-binding agents and optionally neutral salts, such as sodium chloride or sodium sulfate, they produce dyeings in very good color yields with excellent color build-up and consistent shade. One possible procedure is to introduce the material into the warm bath, gradually heat the bath to the desired dyeing temperature, and complete the dyeing process at that temperature. The neutral salts which speed up the

exhaustion of the dyes can also if desired not be added to the bath until the actual dyeing temperature has been reached.

Similarly, the conventional printing processes for cellulose fibers, which can either be carried out in single-phase, for example by printing with a print paste containing sodium bicarbonate or some other acid-binding agent and the colorant, and subsequent steaming at from 100 to 103°C, or in two phases, for example by printing with a neutral or weakly acid print paste containing the colorant and subsequent fixation either by passing the printed material through a hot electrolyte-containing alkaline bath or by overpadding with an alkaline electrolyte-containing padding liquor and subsequent batching of this treated material or subsequent steaming or subsequent treatment with dry heat, produce strong prints with well defined contours and a clear white ground. Changing fixing conditions has only little effect on the outcome of the prints. Not only in dyeing but also in printing the degrees of fixation obtained with dye mixtures of the invention are very high. The hot air used in dry heat fixing by the customary thermofix processes has a temperature of from 120 to 200°C. In addition to the customary steam at from 101 to 103°C, it is also possible to use superheated steam and high pressure steam at up to 160°C.

Acid-binding agents responsible for fixing the dyes to cellulose fibers are for example water-soluble basic salts of alkali metals and of alkaline earth metals of inorganic or organic acids, and compounds which release alkali when hot. Of particular suitability are the alkali metal hydroxides and alkali metal salts of weak to medium inorganic or organic acids, the preferred alkali metal compounds being the sodium and potassium compounds. These acid-binding agents are for example sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium formate, sodium dihydrogenphosphate and disodium hydrogenphosphate.

Treating the dyes of the dye mixtures according to the invention with the acid-binding agents with or without heating bonds the dyes chemically to the cellulose fiber; especially the dyeings on cellulose, after they have been given the usual aftertreatment of rinsing to remove unfixed dye portions, show excellent wet fastness

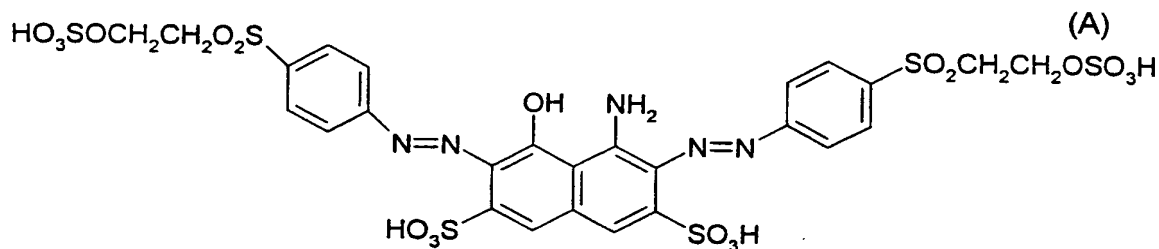
properties, in particular since the unfixed dye portions are readily washed off because of their good cold water solubility.

5 The dyeings of polyurethane and polyamide fibers are customarily carried out from an acid medium. The dyebath may contain for example acetic acid and/or ammonium sulfate and/or acetic acid and ammonium acetate or sodium acetate to bring it to the desired pH. To obtain a dyeing of acceptable levelness it is advisable to add customary leveling assistants, for example based on a reaction product of cyanuric chloride with three times the molar amount of an aminobenzenesulfonic
10 acid or aminonaphthalenesulfonic acid or based on a reaction product of for example stearylamine with ethylene oxide. In general the material to be dyed is introduced into the bath at a temperature of about 40°C and agitated therein for some time, the dyebath is then adjusted to the desired weakly acid, preferably weakly acetic acid, pH, and the actual dyeing is carried out at temperature between 60 and 98°C.
15 However, the dyeings can also be carried out at the boil or at temperatures up to 120°C (under superatmospheric pressure).

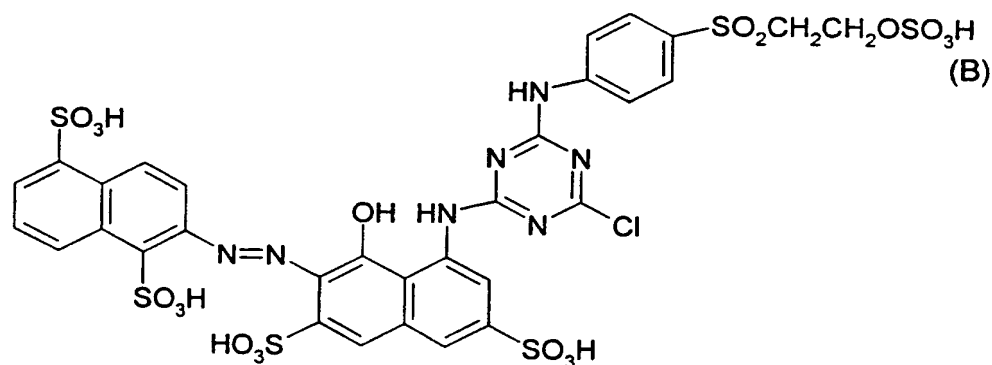
The Examples which follow illustrate the invention. Parts and precentages are by weight, unless otherwise stated. The parts by weight bear the same relation to parts
20 by volume as the kilogram to the liter.

Example 1

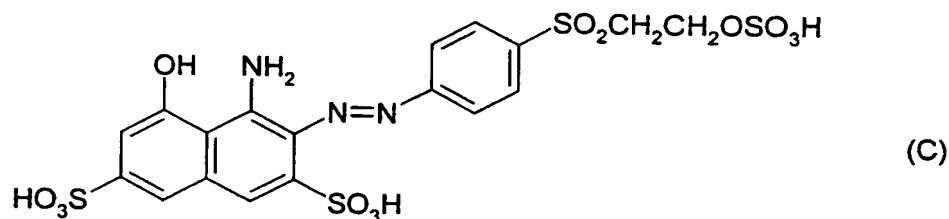
A dye mixture according to the invention is prepared by mechanically mixing 150 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A)



with 33.3 parts of a red electrolyte-salt containing powder with a content of 60% of a dye of formula (B)



with 10 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C)



The resulting mixture contains 75% (w/w) of dye (A) and 20% (w/w) of dye (B) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

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Example 2

A dye mixture according to the invention is prepared by mechanically mixing 155 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 33.3 parts of a red electrolyte-salt containing powder with a content of 60% of a dye of formula (B) with 5.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 77.5% (w/w) of dye (A) and 20% (w/w) of dye (B) and 2.5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

Example 3

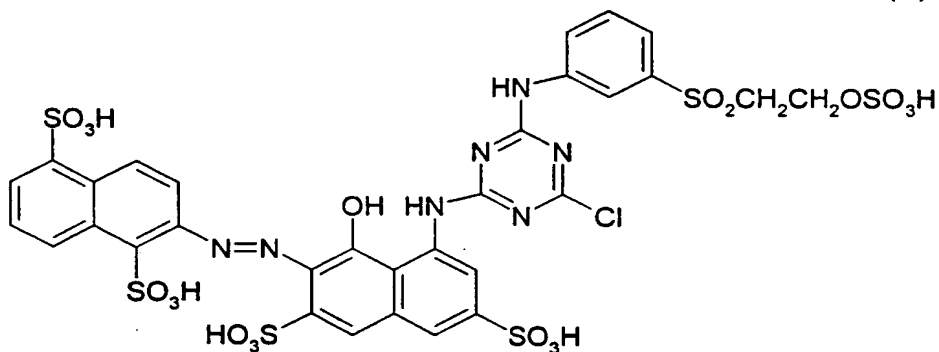
A dye mixture according to the invention is prepared by mechanically mixing 160 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 25 parts of a red electrolyte-salt containing powder with a content of 60% of a dye of formula (B) with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 80% (w/w) of dye (A) and 15% (w/w) of dye (B) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

Example 4

A dye mixture according to the invention is prepared by mechanically mixing 170 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 16.6 parts of a red electrolyte-salt containing powder with a content of 60% of a dye of formula (B) with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 85% (w/w) of dye (A) and 10% (w/w) of dye (B) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

of formula (A) with 28.5 parts of a red electrolyte-salt containing powder with a content of 70% of a dye of formula (E) and with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 75% (w/w) of dye (A) and 20% (w/w) of dye (E) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

(E)



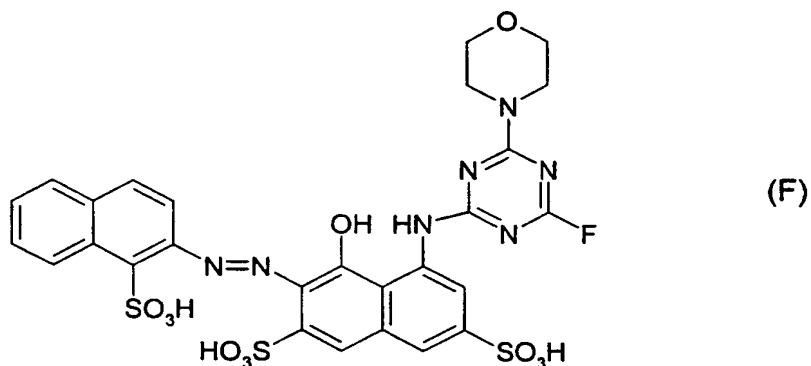
Example 8

A dye mixture according to the invention is prepared by mechanically mixing 160 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 21.5 parts of a red electrolyte-salt containing powder with a content of 70% of a dye of formula (E) and with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 80% (w/w) of dye (A) and 15% (w/w) of dye (E) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

Example 9

A dye mixture according to the invention is prepared by mechanically mixing 160 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 23 parts of a red electrolyte-salt containing powder with a content of 65% of a dye of formula (F) and with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 80% (w/w) of dye (A) and 15% (w/w) of dye (F) and 5% (w/w) of dye (C) and dyes

wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

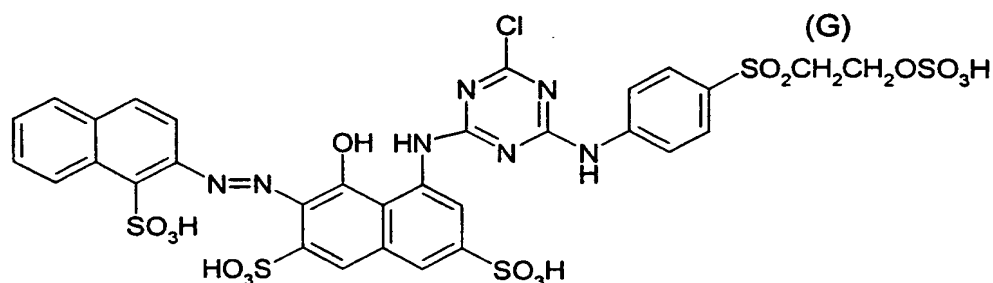


Example 10

A dye mixture according to the invention is prepared by mechanically mixing 170 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 23 parts of a red electrolyte-salt containing powder with a content of 65% of a dye of formula (F). The resulting mixture contains 85% (w/w) of dye (A) and 15% (w/w) of dye (F) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

Example 11

A dye mixture according to the invention is prepared by mechanically mixing 150 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 30.7 parts of a red electrolyte-salt containing powder with a content of 65% of a dye of formula (G) and with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 75% (w/w) of dye (A) and 20% (w/w) of dye (G) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).



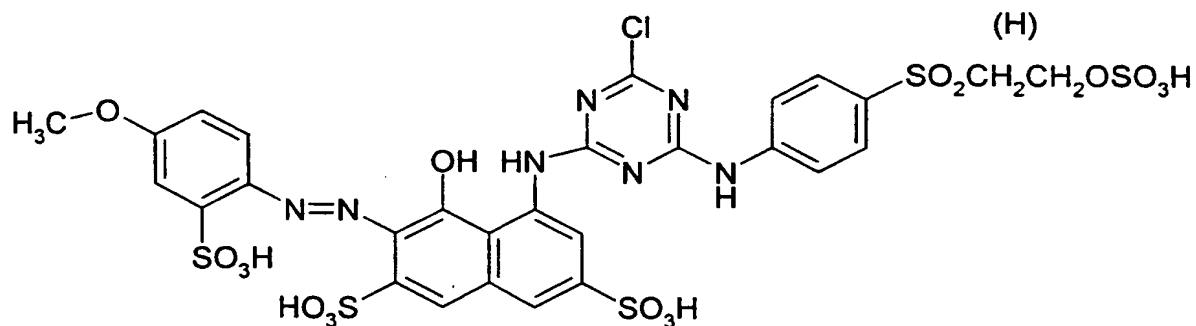
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Example 12

A dye mixture according to the invention is prepared by mechanically mixing 160 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 23 parts of a red electrolyte-salt containing powder with a content of 65% of a dye of formula (G) and with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 80% (w/w) of dye (A) and 15% (w/w) of dye (G) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

Example 13

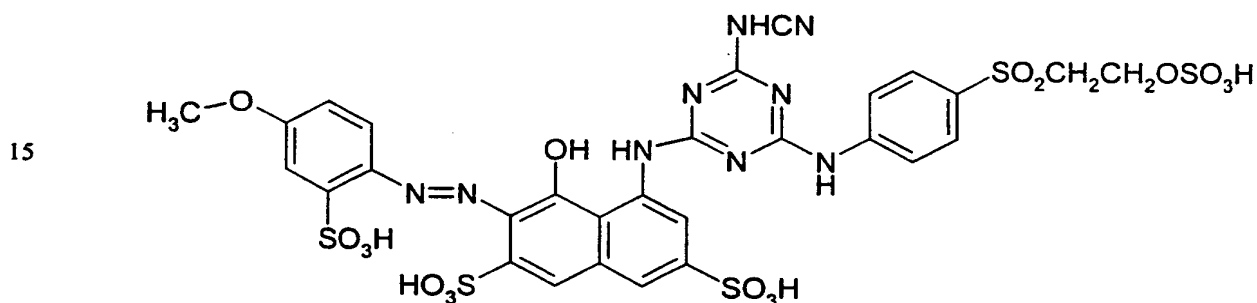
A dye mixture according to the invention is prepared by mechanically mixing 160 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 30 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (H) and with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 80% (w/w) of dye (A) and 15% (w/w) of dye (H) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).



Example 14

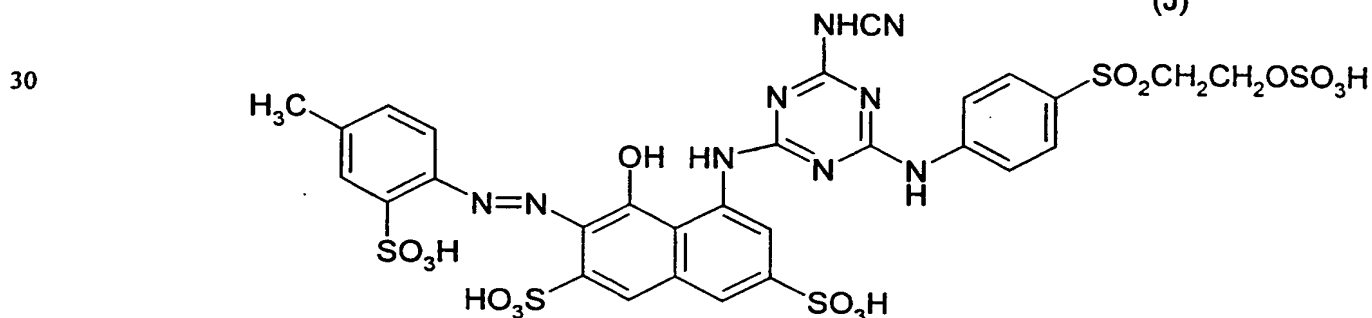
A dye mixture according to the invention is prepared by mechanically mixing 160 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 30 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (I) and with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 80% (w/w) of dye (A) and 15% (w/w) of dye (I) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

(I)

**Example 15**

A dye mixture according to the invention is prepared by mechanically mixing 160 parts of a navy-blue electrolyte-salt containing powder with a content of 50% of a dye of formula (A) with 30 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (J) and with 10.0 parts of a red electrolyte-salt containing powder with a content of 50% of a dye of formula (C). The resulting mixture contains 80% (w/w) of dye (A) and 15% (w/w) of dye (J) and 5% (w/w) of dye (C) and dyes wool in navy-blue shades. The dye mixture exhibits excellent dyestuff properties (i.e. lightfastness and washfastness).

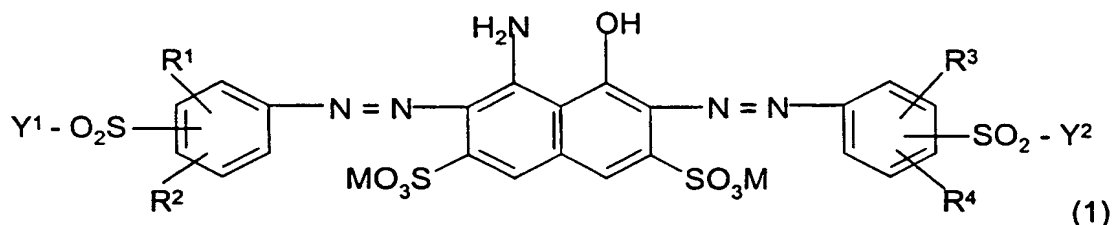
(J)

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What is claimed is:

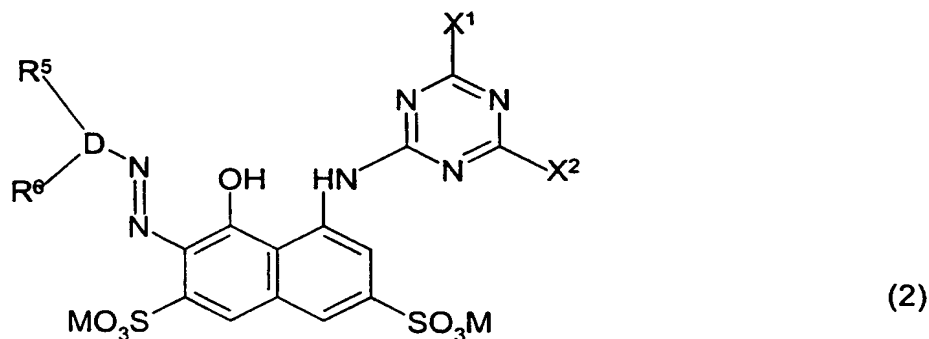
1. A dye mixture comprising one or more, such as one, two or three, disazo dyes conforming to the general formula (1)

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one or more, such as one, two, three or four, monoazo dyes conforming to the general formula (2)

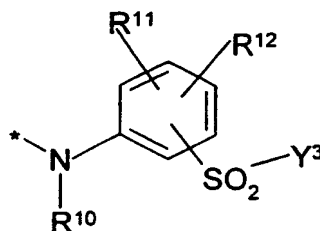
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in which:

- 15 R^1 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy
- R^2 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy
- R^3 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy
- R^4 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy
- R^5 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy
- R^6 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy
- 20 D is a benzene or naphthalene radical;
- X^1 is a fluoro, chloro, cyanamido, or morpholino group or a group of the following formulae; NR^7R^8 or OR^9 or

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wherein

R^7 is hydrogen, C_1 - C_4 alkyl, or C_1 - C_4 alkyl which is substituted by an alkoxy, hydroxy or sulfo group;

R^8 has one of the meanings of R^7 ;

R^9 has one of the meanings of R^7 ;

R^{10} has one of the meanings of R^7 ;

R^{11} is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy

R^{12} is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxy

X^2 has one of the meanings of X^1 ;

Y^1 is vinyl, or is ethyl substituted in the β -position by a substituent which is eliminated by the action of an alkali, forming the vinyl group;

Y^2 has one of the meanings of Y^1 ;

Y^3 has one of the meanings of Y^1 ;

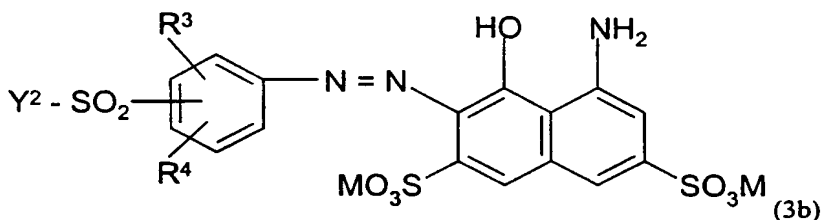
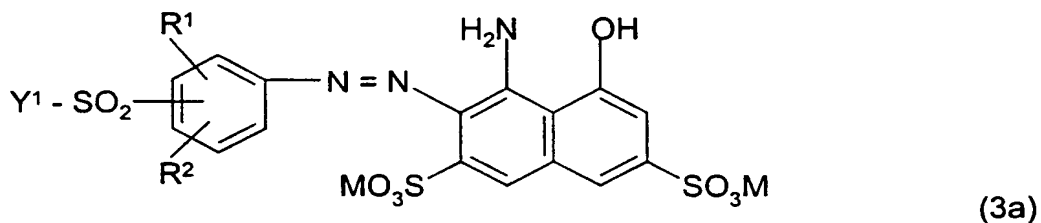
Y^4 has one of the meanings of Y^1 ;

M denotes hydrogen or an alkali metal, such as lithium, sodium and potassium.

2. The dye mixture of claim 1, comprising one or more dyestuffs of the formula (1) in a mixing ratio of 70 to 95% by weight and one or more dyestuffs of the formula (2) in a mixing ratio of 5 to 30% by weight.
3. The dye mixture of claim 1, comprising one or more dyestuffs of the formula (1) in a mixing ratio of 75 to 90 % and one or more dyestuffs of the formula (2) in a mixing ratio of 10 to 25 % by weight.
4. The dye mixture of claim 1, comprising one or more dyestuffs of the formula (1) in a mixing ratio of 75-90 % weight and one or more dyestuffs of the

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formula (2) in a mixing ratio of 8-15 % by weight and one or more dyestuffs of the formula (3a) and (3b) in a mixing ratio of 2-10 % by weight



in which R^1 , R^2 , R^3 , R^4 , M , Y^1 and Y^2 are defined as in Claim 1.

5. A method for the preparation of the inventive dye mixtures in a conventional manner by mechanically mixing the individual dyes in the necessary proportions.

6. A process for dyeing hydroxy- and/or carboxamido-containing fiber material, in which dyes are applied to the material and the dyes are fixed to the material by means of heat or with the aid of an alkali or by means of heat and with the aid of an alkali, which comprises employing as dyes a dye mixture as claimed and defined in claim 1.

INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/EP 00/03150

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B67/22 D06P3/10 D06P1/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 679 697 A (HOECHST AG) 2 November 1995 (1995-11-02) abstract	1-6
Y	EP 0 735 112 A (HOECHST AG) 2 October 1996 (1996-10-02) abstract; examples 13,18	1-6
Y	EP 0 731 145 A (HOECHST AG) 11 September 1996 (1996-09-11) abstract; examples	1-6
A	EP 0 827 987 A (DYSTAR TEXTILFARBEN GMBH & CO) 11 March 1998 (1998-03-11) abstract; examples	1-6
	-/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

25 July 2000

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/03150

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	<p>EP 0 974 622 A (DYSTAR TEXTILFARBEN GMBH & CO) 26 January 2000 (2000-01-26) abstract</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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